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Synthesis and Characterization Studies of L-Valine Barium Chloride NLO Crystal

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Abstract: ***L-valine barium chloride (LVBC), an organic nonlinear optical material was grown by slow evaporation technique at room temperature. The grown single crystal structural information was derived from X-ray Diffraction. The crystal represents the orthorhombic crystal structure. The mode of vibrations of different molecular groups present in LVBC was identified by FTIR studies. The UV-VIS-NIR studies reveal that the crystal has a low UV cut-off of 202.69 nm and has a good transmittance in the entire visible region. The photoluminescence spectra reveal violet emission at 395nm, 430nm, and 437 nm respectively. The second harmonic generation efficiency was determined and is about 0.693 times that of the KDP crystal.***

Keywords: LVBC, Single crystal, PL, SHG

1. Introduction

Nonlinear optical (NLO) materials have attracted considerable attention due to their applications in laser technology, optical communications, optical switching, and optoelectronic device applications. Organic materials are suitable for nonlinear optical devices because of their high nonlinearity when compared to inorganic materials [1-6]. Recently, complexes of amino acids have been explored. Amino acids are interesting materials for NLO applications. The importance of amino acids in NLO applications is because all the amino acids have chiral symmetry and crystallize in noncentro-symmetric space groups. Many natural amino acids are individually exhibiting nonlinear optical properties because they are characterized by chiral carbons, a proton-donating carboxyl (–COOH) group, and the proton-accepting amino (–NH2) group [1, 2, 5]. The crystal structure of L-valine mixed with barium chloride in the ratio of 1:1 was grown from an aqueous solution by the slow evaporation technique. To characterize the above-grown crystals, studies like powder XRD, FTIR, UV–vis transmittance, UV–vis transmittance, PL, and SHG studies were carried out.

2. Synthesis and Crystal growth

LVBC was synthesized from L-valine and barium chloride taken in the mole ratio of 1:1. The calculated amounts of the reactants were thoroughly dissolved in 100ml double distilled water and stirred well for about 5 hours using a magnetic stirrer to ensure a homogeneous solution. The saturated solution was filtered using the Whatmann filter paper. The filtered solution was taken in a perti dish and covered with pinhole polythene cover to restrict the fast evaporation and it is kept in a dust-free compartment for slow evaporation under room temperature. Transparent colorless crystals were harvested in 25 days.

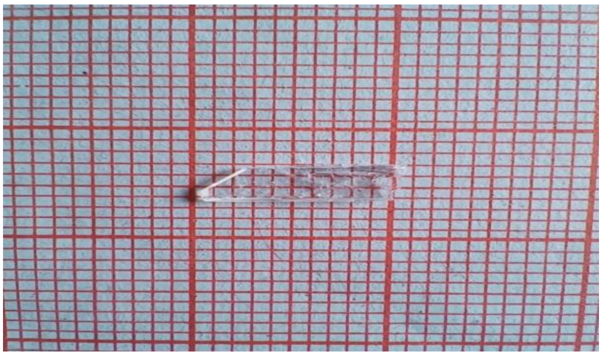

Figure 1: LVBC Crystal

3. Characterization

3.1 Powder X-ray diffraction studies

The crystals have been subjected to powder X-ray diffraction studies to determine the unit cell dimensions and crystalline size. The synthesized grown crystal was scanned over the range from 10° to 80° diffraction angle as shown in Figure 2. The maximum intensity at 9.496 (°2 Theta) angle shows the crystalline nature of the grown crystal. The average crystalline size of a grown LVBC single crystal is calculated by using the Debye Scherrer formula $D = K\lambda / \beta \cos\theta$, Where, D is the average crystalline size, K is a constant value, λ is the wavelength of X-ray (1.540 Å), β is full-width half maximum, and θ is diffraction angle. The average crystalline size of the grown crystal shows 56.61nm [7]. From the data, it is observed that it belongs to the Orthorhombic system with unit cell a=10.85Å, b=9.829Å, c=4.817Å, $\alpha=\beta=\gamma=90°$ [1-6].

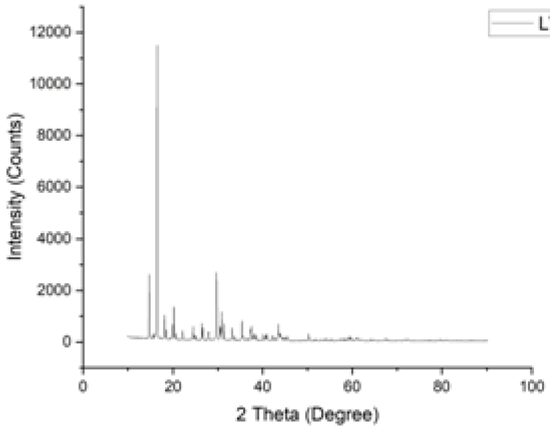

Figure 2: Powder XRD pattern of LVBC

3.2 Fourier Transform Infrared (FTIR) spectral studies

The FTIR spectral analysis of L-valine barium chloride was carried out in the infrared region extending from 500 to 4000 cm-1. The spectrum is shown in Figure 3. Vibrational band assignments of LVBC crystal are tabulated in Table 1. The vibrational band assignments of LVBC crystal prove the presence of expected functional groups in the compound.

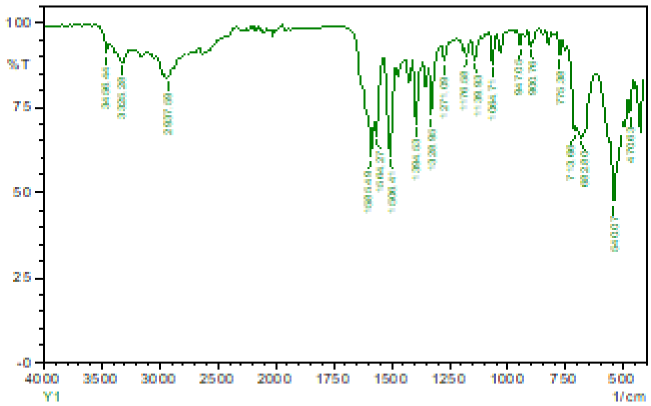

Figure 3: FTIR Spectrum of LVBC

Table 1: Vibrational band assignments of LVBC crystal

S. No	Frequency Cm-1	Vibration assignments
1	470.63	Alkyl halides
2	540.07	coo- stretching
3	682.80	Carboxylic grp of amino acids
4	713.66	coo- stretching
5	775.38	C-H stretching
6	1064.71	C-C-N stretching
7	1139.93	C-C stretching
8	1176.58	C-C stretching
9	1328.95	C-O stretching
10	1394.53	coo- symmetric stretching
11	1506.41	Symmetric deformation of NH3+
12	1585.49	Coo asymmetric stretching
13	2937.59	CH2 asymmetric stretching
14	3325.28	O-H stretching
15	3456.44	N-H stretching

3.3 UV-VIS-NIR Spectral studies

The UV–VIS–NIR spectrum gives information about the molecule through the absorption of UV and visible light. The optical transmission range, transparency cut-off, and absorbance band are the most important optical parameters. The Absorption band of LVBC is observed at 202.69 nm as shown in Figure 4 and there is no absorption band in the entire UV region [1-6]. Hence the crystal is expected to be transparent to the UV-Visible radiation in between these two wavelengths. LAAN is optically transparent in the entire UV region with a 96% transmittance level as shown in Figure 5. and a lower cut-off wavelength at 202.69 nm, is sufficient for laser radiation or other applications in the blue region[1]. LVBC crystals have a good transmission in UV as well as in visible region which is an added advantage for the crystals to be used in optoelectronic applications. The optical direct energy band gap of LVBC crystals is 5.65 eV is determined using Tauc plot energy band gap as shown in Figure 6.

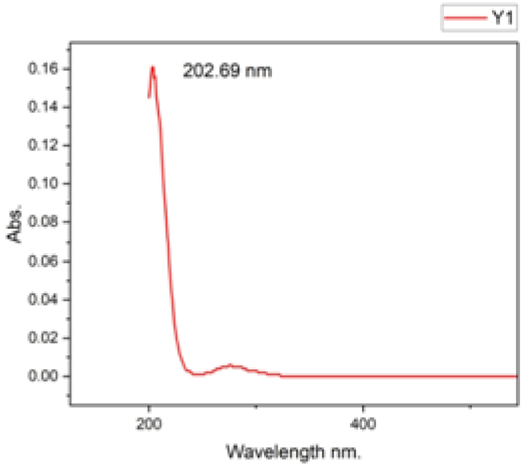

Figure 4: Absorption spectra of LVBC Crystal

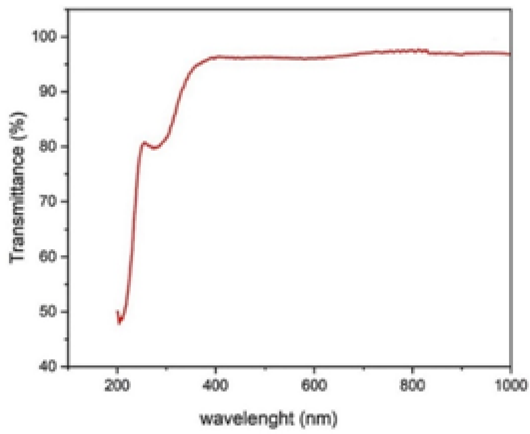

Figure 5: Transmittance of LVBC Crystal

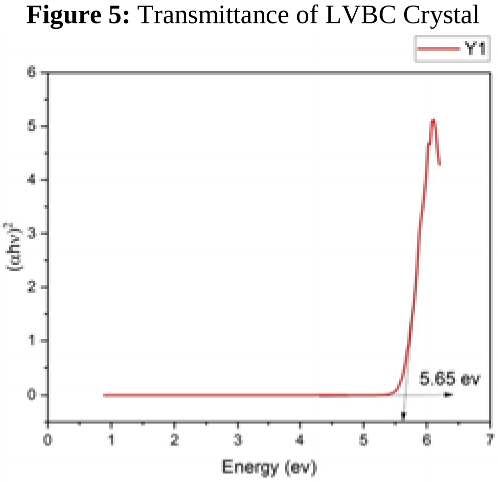

Figure 6: Tauc plot energy band gap of LVBC Crystal

3.4 Photoluminescence studies

PL spectroscopy is a process in which a material absorbs electromagnetic radiation in the system of photons and re-radiates photons. The optical behavior of the title compound was analyzed by PL measurements. Figure 7. shows the emission spectra of LVBC Crystal. The emission peak with maximum intensity was obtained at 437 nm [3]. The peaks rise in UV emission. The emission peaks observed at 437 nm show violet emission. Violet emission has been obtained at 395nm, 430nm, and 437 nm.

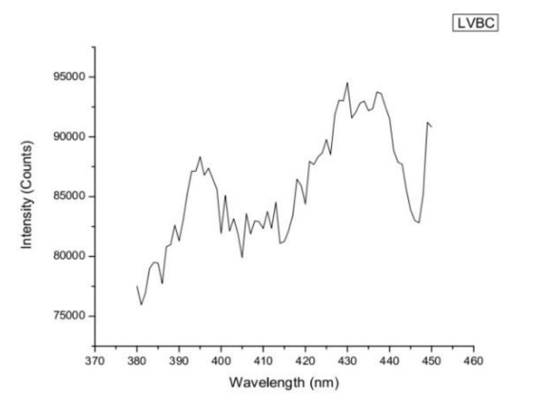

Figure 7: PL spectra of LVBC crystal

3.5 Second harmonic generation efficiency studies

A fundamental laser beam of 1064 nm wavelength (6 ns pulse width with 10Hz pulse rate) from an Nd-YAG laser was made to fall normally on the sample cell. The incident wavelength of the light is 1064 nm. The wavelength of the light emitted from the sample is 532 nm [1-6]. KDP crystals were powdered to an identical size and were used as reference materials in the SHG measurement. The SHG efficiency of LVBC crystal was found to be 0.693 times that of KDP crystal.

4. Conclusion

Colorless and transparent Single crystals of L-valine barium chloride (LVBC), have been grown by slow evaporation method at room temperature. Powder X-ray diffraction studies were carried out to calculate the lattice parameters of the grown crystals. From the data, it is observed that it belongs to the Orthorhombic system with unit cell parametersa=10.85Å, b=9.829Å, c=4.817Å, α=β=γ=90° and the average crystalline size of the grown crystal shows 42.73 nm. The FTIR spectrum confirmed the amino group in the compound. UV–VIS–NIR spectra reveal that the absorption band of LVBC is observed at 202.69 nm. LVBC is optically transparent in the entire UV region with a 96% transmittance level and lower cut-off wavelength at 202.69nm. The optical energy band gap of LVBC crystals is 5.65eV are determined. PL spectra show the emission peak with maximum intensity was obtained at 437 nm. The peaks rise in UV emission. The emission peaks observed at 437 nm show violet emission. The SHG studies show that the SHG efficiency of LVBC crystal was found to be 0.693 times that of KDP crystal. Based on these facts we propose the title compound L-valine barium chloride (LVBC) as a novel organic material for NLO applications

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